The University of Chicago

THE ADSORPTION OF VAPORS AT LOW PRESSURES

A DISSERTATION

SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

AMANDO CLEMENTE

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Besides the time devoted to the problem discussed in this dissertation, Mr. Clemente devoted the greater part of his time during three Quarters to work on War Problems under the guidance of Professor Harkins.

JULIUS STIEGLITZ
Chairman of the Department of Chemistry

R. UNIV.
BIBLIOTHEEK
LEIDEN

THE ADSORPTION OF VAPORS AT LOW PRESSURES

OBJECT

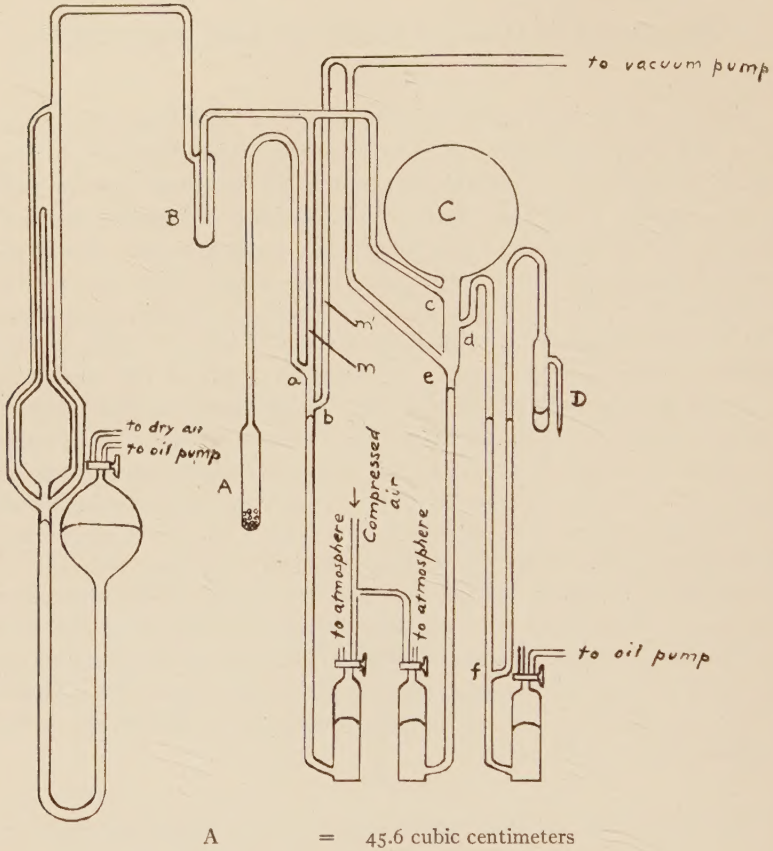
The power of charcoal to adsorb gases has been known for many years, and considerable amount of work on the subject has been done by various investigators. Of those who have given important contributions to the solution of different phases of the problem, Chappius,[1] Hunter,[2] Travers,[3] Miss Humphrey,[4] and Titoff[5] may be mentioned. The application of the process in the preparation of gas masks which were used in the recent Great War seems to have aroused in the chemists and physicists of today greater interest in the problem, which is now under investigation in different laboratories. An extensive study of the adsorption of carbon dioxide and ammonia by charcoal at widely varying temperatures and pressures has lately been made by Richardson.[6] While Langmuir[7] and Williams[8] have presented theoretical papers on adsorption, the former based his ideas on the kinetic theory, and the latter arrived at his conclusions from thermodynamic principles. Of the available data on the subject, there is no record of measurements made at low pressures, except those of Lemon[9], which, however, are not recorded much below 0.001 mm. The present work on the adsorption of charcoal at low pressures has been undertaken in an attempt to establish the relation between the power of charcoal to adsorb and the size of its pores. The problem was started as a part of an investigation made at the request of the National Research Council.

APPARATUS

The device used in this work is shown in the diagram in Figure 1. With the exception of the Macleod gauge, all parts of the apparatus are made of pyrex glass. Pressure between 0.00001 and 0.50 mm. of mercury are read in the Macleod gauge, which has a volume of 500 cc., and of which the capillary part is calibrated to 0.01 cc. Higher pressures are measured by means of a cathetometer from the difference between the

[1] *Ann. Phys.* (3), **12**, 160 (1881).
[2] *J. Am. Chem. Soc.*, **25**, 649 (1872).
[3] *Proc. Roy. Soc.*, A, **78**, 9 (1906).
[4] *Z. Physik. Chem.*, **74**, 129 (1910).
[5] *Ibid.*, **74**, 641 (1910).
[6] *J. Am. Chem. Soc.*, **39**, 1828 (1917).
[7] *Ibid.*, **40**, 1361 (1918).
[8] *Proc. Roy. Soc. Edinburgh*, **38**, 23 (1919); Proc. Roy. Soc., A, **96**, 287 (1919).
[9] *Phys. Rev.* **14**, 394 (1919).

heights of the mercury levels in the tubes (m) amd (m') which serve as manometer arms, (m') being open to the vacuum pump. The bulb A



A	=	45.6	cubic centimeters
B	=	85.3	" "
C	=	1022.8	" "
Gauge	=	586.5	" "
Connecting tubes	=	207.3	" "

Volume of the system = 1947.5 CC.

FIG. 1

contains one gram of charcoal. It can be opened to, or shut off from, the system by bringing the mercury level in (m) below or above the side arm (a). The trap B is inserted in order that the vapor in the system may

be liquified and the air dissolved in it either measured or removed as the case may demand. *C* is a gas reservoir, which has been inserted in the system for the purpose of reducing the pressure of the vapor admitted in the apparatus. It can be sealed by mercury at (*c*), (*d*) and (*e*). Bulb *D* holds the liquid whose vapor is used as adsorbate. It opens to the main portion of the apparatus at (*f*). The whole system can be opened to, or shut off from, the mercury diffusion pump by means of the mercury seals at (*b*) and (*e*). These mercury seals are found to be very handy in the present work; for they take the place of stopcocks, which are very inconvenient, not only because they give rise to leaks, but also on account of the fact that their grease is also a constant source of trouble especially when it is soluble in the gas or vapor under investigation.

MATERIALS

Charcoal number 4, made from cocoanut shells and supplied by Dr. N. K. Chaney, of the National Carbon Company, was used in this work. It consists of small granules eight to fourteen mesh. The benzene was thiophene free and was dried by treatment with metallic sodium.

METHOD OF PROCEDURE

The first step in the process consists of outgassing the charcoal. This is effected by opening the system at (*c*) and (*e*) to the mercury diffusion pump. The charcoal in bulb *A* is gradually heated to 550° C and is kept at that temperature until the pressure reading becomes constant at less than 0.00001 mm. The process of outgassing requires from five to ten hours. It can, however, be considerably shortened by raising the temperature of the charcoal to about 650° C for two or three hours during the process. As a rule a fresh sample of charcoal is much more difficult to outgas than a sample which has previously been outgassed, since it only takes about six hours, generally, to outgas completely one gram of charcoal for the second time.

After the charcoal has been thoroughly outgassed, bulb *A* is shut off from the system by manipulating the mercury seal at (*a*) before bulb *A* has had any time to cool. In this way any trace of air which may remain in the system is prevented from being adsorbed by the charcoal when it cools down to room temperature, 20° C more or less. The required amount of benzene vapor is introduced into the system by opening the mercury seal at (*f*), and letting some benzene vapor from *D* enter the system.

The benzene vapor admitted in the apparatus is frozen in trap *B* by

means of liquid air, and any trace of air which it may still contain, after the treatment it has undergone, is pumped out. Said treatment consists of boiling off about three-fourths of the liquid originally put in *D*. Then *D* is immersed in liquid air to freeze the benzene it contains and the air is pumped out by opening the mercury seals (*e*) and (*f*) thus communicating bulb *D* with the vacuum pump until the pressure is brought down to less than 0.00001 mm. Then *D* is again sealed from the rest of the system, and the liquid is distilled back and forth (*n*) and *D* by alternately warming and immersing the latter in liquid air. The liquid is finally frozen in *D* and the air pumped out as previously. This procedure is repeated several times; but even then, about 0.00005 mm. of air is found present in 5.00 mm. of benzene occupying a volume of 1950 cc. at 20.0° C. In this process there is no danger of losing much benzene, because its vapor pressure at liquid-air temperature is only about 0.000005 mm.

After removing the air from the benzene, the liquid-air bath is removed from *B*, and the pressure of the benzene vapor is read as soon as the temperature of *B* becomes the same as the room temperature. Then *A* is opened to the system, and the pressures are read at definite intervals of time until equilibrium is reached, i.e., when the pressure becomes constant for at least one hour.

At low pressures the point of equilibrium between the adsorbed and the unadsorbed vapor is established only after the charcoal has been in contact with the vapor for at least six hours. The final reading of the equilibrium pressure, however, is not taken in less than twenty-four hours; and in a few cases an allowance of forty-eight hours was made for equilibrium to be established. The considerable length of time which is necessary for the attainment of equilibrium between the adsorbed and the free benzene vapor does not agree at all with the common experience and the general belief that adsorption equilibrium is reached in a very short time. Richardson,[1] however, observed that when a new sample of gas was admitted into his system, pressure did not become constant within a reasonable amount of time according to his judgment. He further noted that the values of pressures obtained at definite temperatures when the temerature was falling were not coincident with the pressures at the same temperatures when the equilibrium pressures were taken when the temperature was rising. An explanation to this phenomenon will be given later.

To be certain that the equilibrium point in the system adsorbed benzene and benzene vapor has been attained, bulb *A* is shut off from the

[1] *Loc. cit.*

system after the pressure has become constant, and the negligible quantity of unadsorbed vapor is pumped out, and the pressure of the system is brought down to less than 0.000005 mm. Then bulb *A* is again opened to the system and the charcoal is allowed to give off some of the vapor which it has adsorbed. In this way the equilibrium pressures obtained from a decreasing pressure is checked by an equilibrium pressure reached from a low pressure point.

EXPERIMENTAL RESULTS

The results obtained are given in the following tables. The volume of the vapor adsorbed expressed in cubic centimeters under standard conditions are calculated from the known volume of the system, the temperature of the experiment, and the difference between the total pressure P and the equilibrium pressure p, which represents the pressure that would be exerted by the benzene vapor in the charcoal if it were released.

TABLE I

Charcoal No. 4*a*—Benzene Temperature 21.0° Pressure in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.380	0.018	0.362	0.77
0.72	0.028	0.682	1.28
1.062	0.040	1.042	2.01
1.428	0.060	1.368	2.79
1.808	0.064	1.744	3.81
2.184	0.068	2.116	4.39
2.556	0.068	2.488	5.13
2.958	0.072	2.886	5.97
3.366	0.072	3.294	6.84
3.674	0.076	3.598	7.48
4.058	0.076	3.982	8.31
4.452	0.076	4.376	9.14
4.806	0.076	4.730	9.89
12.076	0.088	11.988	25.51
25.654	0.144	25.644	54.61
32.804	0.256	32.348	69.50
43.38	0.66	42.698	89.50

TABLE II

Charcoal No. 4a—Benzene Temperature 20.5° C Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.032	0.00006	0.032	
0.094	0.008	0.086	0.18
0.158	0.012	0.146	0.39
12.136	0.026	12.100	22.72
22.280	0.076	22.204	47.42
23.964	0.096	23.868	50.93
26.178	0.120	26.058	55.26
28.688	0.168	28.520	60.60
32.070	0.232	31.838	67.67
35.858	0.380	35.478	75.15
39.158	0.690	38.468	81.64

TABLE III

Charcoal No. 4a—Benzene Temperature 21.5° C. Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.036	0.00006	0.036	0.077
0.33166	0.00010	0.3316	0.62
0.4716	0.00012	0.4715	1.00
0.8973	0.00036	0.8969	1.91
1.5966	0.00100	1.5956	3.486
1.8756	0.00104	1.8745	4.01
2.2545	0.00110	2.2534	4.83
6.5644	0.00180	6.5626	14.28
14.2326	0.0068	14.2254	30.57
22.2958	0.0400	22.2258	47.39
27.4958	0.0960	27.3998	58.24
33.4098	0.2400	33.1698	70.36
39.7998	0.6500	39.1498	82.56

TABLE IV

Charcoal No. 4a—Benzene Temperature 21.0° C. Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.06244	0.00032	0.06212	0.134
0.12292	0.00034	0.12248	0.260
0 18002	0.00036	0.18066	0 384
0.26162	0.00038	0.26124	0.556
0.37892	0.00046	0.37840	0.803
0 49014	0.00054	0.49560	1.060
0.80780	0.00066	0.80714	1.728
1.12904	0.00072	1.12832	2.402
1 43152	0.00076	1.43076	3.042
1.81036	0.00082	1.80954	3.915
3.74954	0.00110	3.74844	8.085
7.80854	0.00180	7.80674	16.41
18.86674	0.01600	18.85074	40.21
25.93074	0.0640	25.86674	55.42
33.10674	0.200	32.90674	70.26
41.06674	0.620	40.40674	86.28

TABLE V

Charcoal No. 4a—Benzene Temperature 20.3° C. Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.04404	0.00004	0.04400	0.094
0.10648	0.00005	0.10643	0.228
0.23252	0.00007	0.23245	0.498
0.45157	0.00010	0.45147	0.968
0.57289	0.00015	0.57274	1.234
0.80121	0.00026	0.80095	1.728
1.13135	0.00050	1.13085	2.440
1.60285	0.00080	1.60205	3.450
2.02341	0.00100	2.02241	4.349
2.53241	0.00120	2.53121	5.444
4.83121	0.00140	4.82981	10 31
15.84981	0.00740	15.84241	34.17
26.40241	0.0440	26.35841	56.44
39.21801	0.3864	38.83161	83.81
49.56161	1.80	47.76	103.0
75.642	11.89	63.75	137.2
85.20	21.36	63.84	138.4
100.10	34.86	65.24	140.7
114.92	48.84	66.08	142.3
127.78	60.88	66.90	143.2
144.14	74.54	67.60	145.7
149.95	75.68	74.27	103.8
173.21	75.70	97.61	210.3

TABLE VI

Charcoal No. 4a—Benzene Temperature 22.0° C Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.29960	0.00003	0.29957	0.641
0.71279	0.00003	0.71276	1.527
1.17716	0.00004	1.17712	2.523
2.53712	0.00006	2.53706	5.437
12.54706	0.00320	12.54386	27.05
19.33386	0.02000	19.31386	41.66
27.85586	0.100	27.84586	59.69
41.42586	0.780	40.64586	85.47

TABLE VII

Charcoal No 4a—Benzene Temperature 24.0° C Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.2916	0.000015	0.2916	0.646
0.48296	0.000015	0.48295	1.069
0.79714	0.00002	0.79712	1.766
1.50024	0.00002	1.50022	3.323
2.76022	0.00004	2.76018	6.113
5.13022	0.00004	5.13018	11.36
10.39022	0.00120	10.38902	22.49
15.36022	0.0090	15.35122	34.02

TABLE VIII

Charcoal No. 4a—Benzene Temperature 23.0° C. Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
0.2684	0.00001	0.2684	0.596
1.2884	0.000015	1.2884	2.863
6.9084	0.00030	6.9081	15.36
11.9484	0.0050	11.9434	26.83

TABLE IX

Charcoal No. 4a—Benzene Temperature 20.5° C Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
2.53	0.000015	2.53	5.692
5.42	0.000045	5.42	12.19
7.86	0.000032	7.86	17.68
10.57	0.00124	10.57	23.78
16.33	0.00810	16.32	36.74
22.26	0.0390	22.22	50.08
30.48	0.1998	30.28	68.11
40.16	1.23	38.94	87.54
51.88	6.07	45.81	104.5
67.12	19.44	47.68	107.3
88.80	38.98	48.82	109.8
114.11	63.68	50.43	113.4
121.00	70.56	50.44	113.4

TABLE X

Charcoal No 4b—Ethyl Alcohol Temperature 20.0 °C. Pressures in Mm. of Mercury		$(P-p)$	Vapor Adsorbed in Cc. at 0°C. and 760 Mm. per Gram Charcoal
Total P	Equilibrium p		
5.98	0.0162	5.96	13.26
11.34	0.072	11.27	25.09
21.20	0.370	20.83	46.19
35.67	1.06	34.61	76.76
49.27	2.12	47.15	104.6
68.67	7.86	60.81	134.8
98.13	30.80	67.33	149.3

DISCUSSION OF RESULTS

Various theories have been proposed to account for the nature of adsorption and several formulas expressing the relation between the equilibrium pressure and the concentration of the substance adsorbed have been proposed. The only formula, however, which applies to the majority of cases of adsorption of gases by charcoal is

$$C = ap^{1/n}$$

where C represents the number of cubic centimeters of the gas adsorbed by one gram of charcoal, a the number of cubic centimeters adsorbed at

1.00 mm. pressure, and $1/n$ is a quantity which depends upon the nature of the adsorbent and adsorbate. It is equal to $\frac{d \log C}{d \log p}$.

Although the formula expresses in a general way the relation between the equilibrium pressure and the concentration of the vapor adsorbed, it does not hold in cases where $\frac{d \log C}{d \log p}$ is a variable. As a matter of fact, it

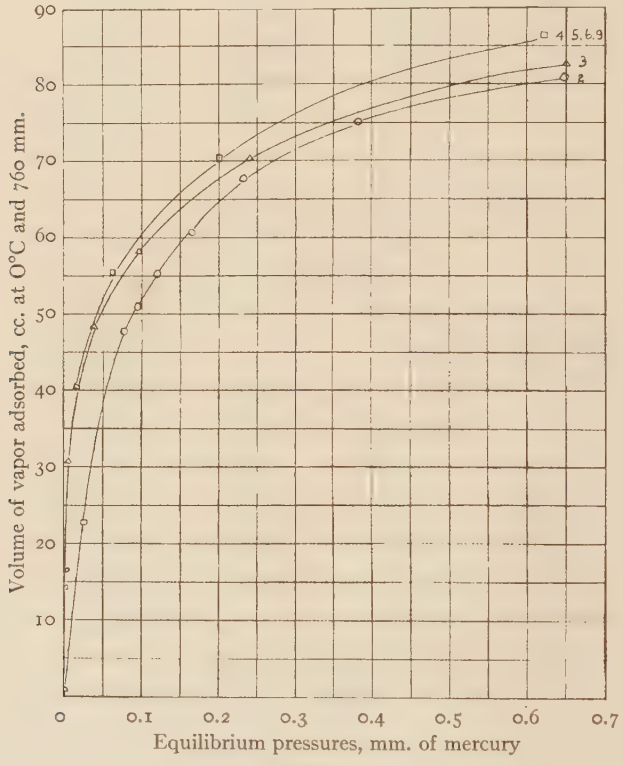


FIG. 2

has been found by Richardson to decrease with increasing equilibrium pressures, which is verified by the experimental results obtained here. Since the nature of the curve produced by plotting the equilibrium pressure against the volume of the vapor adsorbed is the same in all known cases as can be seen in Figure 2, it might be possible to find another mathematical expression that will apply more exactly to all cases of adsorption equilibrium.

The relation between the adsorbed vapor and equilibrium pressure in this series of experiments is similar to those obtained by previous investigators in spite of the great difference in pressures. It is interesting to note the fact that the volume of the vapor adsorbed by one gram of charcoal in these experiments has very nearly the same value at the saturation point as that obtained by Richardson in the case of carbon dioxide and ammonia, as the following figures in Table XI show.

TABLE XI

Temp. C°	Substance	Cc. Adsorbed per Gram Charcoal	Number of Molecules Adsorbed per Gram Charcoal	Pressure Mm.
−20°.....	NH_3	152.9	4.21×10^{21}	1530
−64°.....	CO_2	107.1	2.95×10^{21}	1176
20.3°.....	C_6H_6	143.2	3.94×10^{21}	74.54
20.0°.....	C_2H_5OH	144.5	3.98×10^{21}	30.80

Of course the foregoing results cannot be expected to be in perfect agreement with each other on account of the widely differing conditions under which the experiments were made; yet they seem to suggest that the number of molecules which a gram of charcoal can adsorb is the same for all substances if the size of their molecules is the same. Furthermore, assuming that the charcoal becomes covered with a monomolecular layer of benzene vapor at the point where the curve in Figure 3 begins to deflect the quantity 2.31×10^{21} is obtained as equal to the number of molecules in a monomolecular layer of benzene covering the surface of the charcoal. From this number of molecules the surface exposed by one gram of charcoal is calculated to be 1.3708×10^{8} sq. cm., or 13708 square meters. This area was obtained from the length of one edge of the benzene molecule, assuming it to be cubical in shape, and calculating the size of the molecule from its density and molecular volume.

The number of molecules of vapors adsorbed by one gram of charcoal when air saturated with vapor was passed through a column of charcoal in our tests was 2.226×10^{21} for chlorpicim and 2.125×10^{21} for isobutyric acid. The agreement in the order of magnitude of the number of molecules adsorbed by charcoal under very different experimental conditions not only confirms the view in regard to the number of adsorbed molecules which a gram of charcoal can hold, but it also seems to show that the surface exposed by one gram of charcoal as calculated above is not far from the true value.

The results given in Tables I, II, III, IV, and V, as well as the graphs in Figure 2, show slight differences, which can be accounted for by the fact that due to some imperfections of the apparatus in the early part of the work air could not be completely removed from the benzene vapor,

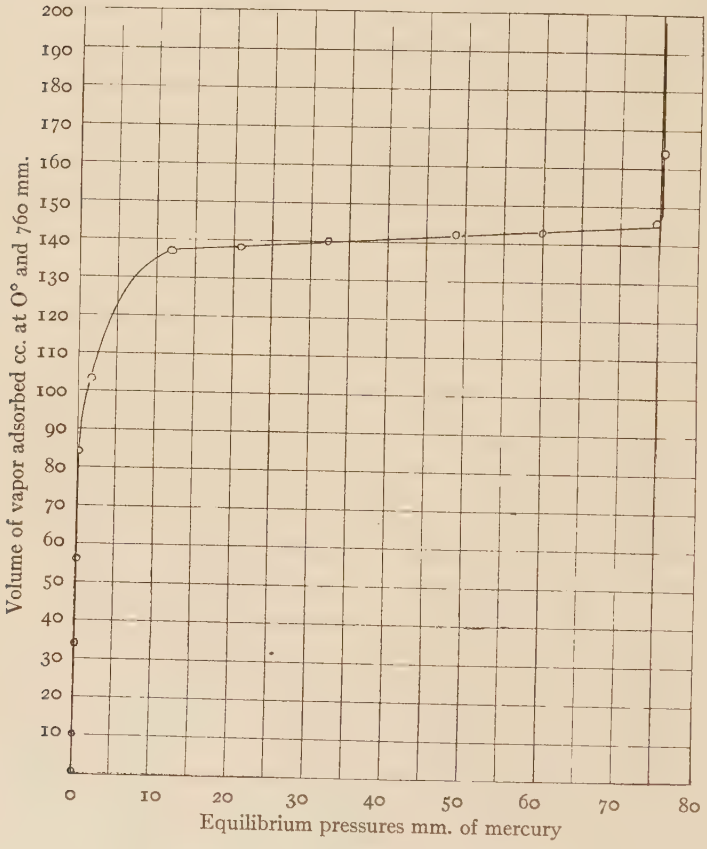


FIG. 3

which, naturally, gave equilibrium pressures greater than they should be. The discrepancy being proportional to the amount of air present in the system. Concordant results, however, were obtained, as given in Tables VI, VII, VIII, and IX, after the device for removing traces of air in the adsorbate was introduced in the apparatus.

It was pointed out previously that contrary to the expectation and

common experience of workers on adsorption, it required a considerable length of time before equilibrium pressure was reached at low pressures. With such an irregular surface as that possessed by charcoal, it is not by

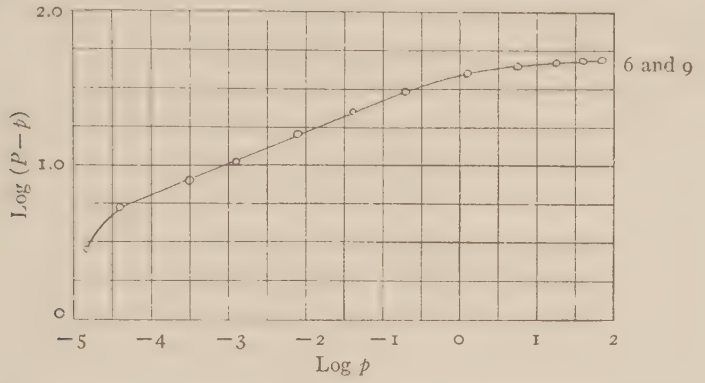


FIG. 4

any means surprising to find the equilibrium between the adsorbed vapor and free vapor to be established after a long time. In case of plane surfaces, like glass and mica, which were investigated by Langmuir,

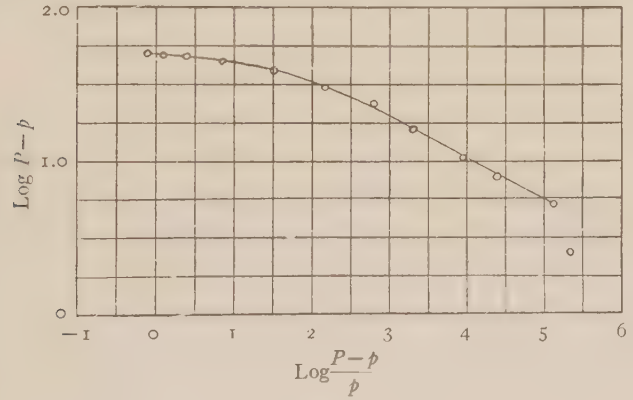


FIG. 5

adsorption equilibrium is attained within a short period of time, because the elementary surfaces of the adsorbent are equally exposed to the molecules of the adsorbate with which it comes in direct contact. The condition, however, in the case of charcoal is very different. Due to the

irregularity of the surface, a point of metastable equilibrium, as has been noted in the course of these experiments, is reached, and the pressure would remain constant for one or two hours. This equilibrium point, nevertheless, exists only between the free vapor and that adsorbed by the outer surface of the charcoal. The term "outer surface" is used here to distinguish it from the surface of the inner structure, which very likely does not come directly in contact at any time with the free vapor of the adsorbate; for the way to it is obstructed by some of the molecules adsorbed by the outer surface of the charcoal. True equilibrium, therefore, does not exist between the adsorbed vapor and free vapor in

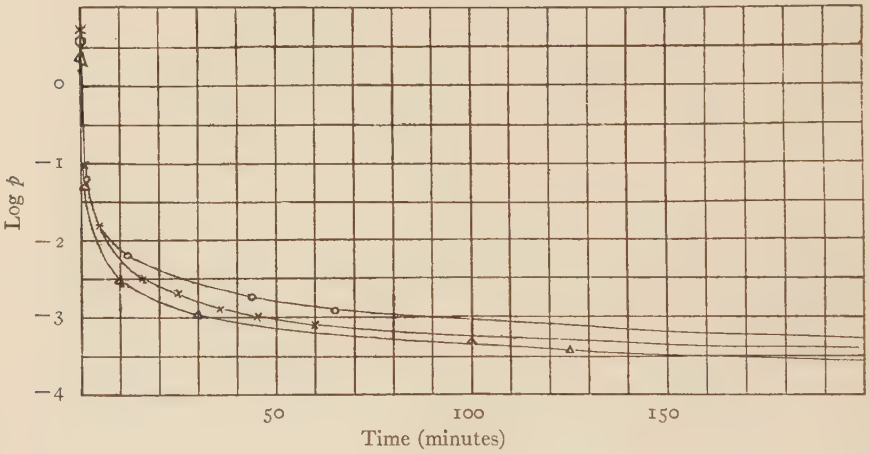


FIG. 6

the system until the inner surface of the irregular structure of the charcoal gets hold of its share of adsorbed molecules, which according to the existing conditions could only be attained with great difficulty so that a very long time is needed for its attainment. We can have an idea of the mechanism of this slow process if we take into account the fact that the molecules held by the outer surface have a better chance to pass into the vapor phase than to diffuse into the inner structure of the charcoal.

There is no doubt but that the same slow process goes on at high equilibrium pressures. The difference, however, between the metastable and the true equilibrium pressures becomes negligible after the greater portion of the inner surface becomes covered with adsorbed molecules; so that at high pressures the equilibrium condition of the system is apparently attained within a very short period of time.

SUMMARY

The equilibrium pressures of benzene and ethyl alcohol vapors in contact with charcoal were measured at pressures ranging from 0.00001 to 75.00 mm. of mercury. The curves representing the results obtained have the general characteristics of the logarithmic curves, which Richardson and other workers on the subject have found to hold fairly for other gases and vapors.

The length of time which is required to attain equilibrium condition at low pressures has been accounted for as due to the difficulty that the vapor molecules encounter in getting into the inner structure of the very irregular surface of the charcoal.

In concluding this work, I wish to express my sincere thanks and appreciation to Professor W. D. Harkins for his suggestions and criticisms, as well as for the valuable help he has given me to facilitate the performance of the experiments.